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CORROSION OF METALS IN DEIONIZED WATER AT 38° C (100° F)

by Barbara A. Johnson

Lewis Research Center

Cleveland, Ohio

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ABSTRACT

The corrosion of copper, cadmium, tungsten, and Mallory-1000 is discussed. Mention is made of 304 stainless steel, 1100 aluminum, titanium, tantalum, silver, and boron steel, all of which showed no corrosion. The importance of corrosion in nuclear reactor cooling water is discussed. Data were obtained by chemical analyses of the water rather than from physical measurement of the test specimen.

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SUMMARY

The corrosion of 10 metals and alloys in deionized water at 38° C was determined. Titanium, 1100 aluminum, 304 stainless steel, boron steel, silver, and tantalum showed no corrosion in deionized water. Cadmium, Mallory-1000, tungsten, and copper exhibit corrosion at this temperature. In nuclear applications, chemical analyses of the water in which test specimens are immersed provide more useful corrosion information than does physical measurement of weight loss.

INTRODUCTION

The corrosion of metals is caused by the attack of the environment on the metal. The extent of attack with time is termed corrosion rate. Corrosion is normally determined by measuring specimen weight loss.

However, in nuclear reactor applications measurement of corrosion by specimen weight loss may not have the sensitivity to detect that metals and alloys are being dissolved in the reactor cooling water to produce operational problems. Activation of small amounts of certain ions causes a large increase in radiation levels. It has been found that colorimetric analysis of the water provides more useful information.

Studies have been made of the corrosion of tungsten, cadmium, 304 stainless steel, 1100 aluminum, titanium, tantalum, boron steel, silver, copper, and Mallory-1000 (90 percent W, 6 percent Ni, and 4 percent Cu) in deionized water at 38° C using both colorimetric analyses and weight loss.

According to Wilkinson and Murphy (ref. 1) there is no reaction between solid cadmium and boiling water. The Handbook of Chemistry and Physics (ref. 2) lists tungsten and copper as insoluble in water. However, in this study, colorimetric analyses of the water have shown that cadmium, copper, Mallory-1000, and tungsten do dissolve in amounts significant in nuclear applications. The corrosion determined by specimen weight loss would be negligible except for Mallory-1000.

EXPERIMENTAL

The specimens were cleaned in a chemical polish specific for the material (ref. 3). They were weighed and the total area calculated.

Each specimen was suspended in 2 liters of deionized water in a closed Erlenmeyer flask fitted with a cold finger condenser. Duplicate tests were run at 38° C with the exception of copper. One copper test was run at 43° C, the other at 38° C. The system was static except for heat convection. Twenty-five milliliters of solution were withdrawn every 24 hours and stored in a polyethylene bottle until the analyses were made. Standard colorimetric analyses (ref. 4) were used to determine the concentration of material present.

DISCUSSION AND RESULTS

Table I gives the duration of each test and the results. The colorimetric procedure used is also indicated. The duration of each test varied according to corrosion characteristics of each material being studied.

The total amount of each element found in the water each day was determined by analyzing a 25-milliliter sample. The amount of metal present in the total volume of solution was then calculated. This value was then increased by adding to it the amount of metal present in each of the 25-milliliter samples taken previously. Hence, the total

TABLE I. - DURATION AND RESULTS OF TESTS

Metal ion	Duration of test, days	Colorimetric procedure used (coloring reagent)	Results
Tantalum	24	Pyrogallol	No dissolution observed
Titanium	17	Hydrogen peroxide	No dissolution observed
1100 Aluminum	10	Extraction of aluminum hydroxyquinolate with chloroform	No dissolution observed
Boron steel	18	Quinalizarin in concentrated sulfuric acid to complex boron	No dissolution observed
Silver	47	Diethylaminobenzylidenerhodanate	No dissolution observed
304 Stainless steel	10	1-10-0-phenanthroline complex of iron	No dissolution observed
Tungsten	42	Sulfuric acid in hydroquinone	Dissolution (fig. 1(c))
Mallory-1000	37	Sulfuric acid in hydroquinone to complex tungsten	Dissolution (fig. 1(d))
Copper	36	Alkaline extraction with diethyldithiocabamate	Dissolution (fig. 1(a))
Cadmium	22	Extraction of red cadmium dithizonate	Dissolution (fig. 1(b))

amount of metal released from the sample was determined.

Figures 1(a) to (d) are plots of the total amount released per unit area against the duration of the test. These plots represent the corrosion of the various specimens. Numbers 1 and 2 refer to duplicate tests. The upper curve of the copper plot represents corrosion at 43° C, while the lower curve represents corrosion at 38° C.

The shape of the copper and cadmium curves indicates that a protective film develops, thereby hindering further dissolution. Physical examination of the specimens revealed an adherent oxide film which is characteristic of protective oxide formation. The Mallory-1000 and tungsten curves indicate a nonprotective film and possibly autocatalysis which produces continued dissolution. The oxide films of these specimens were nonadherent.

The disagreement between the tungsten tests has not been explained although different colored oxides were formed on each specimen. The significant point is the shape of the two curves, both showing a nonprotective film.

The loss of weight found for copper using the weight change method was 0.5 milligram. Colorimetric analysis of the water gave 2.4 milligrams of copper in solution. The weight change method gave 304 milligrams of Mallory-1000 lost during the test. Colorimetric analysis of the water showed 340 milligrams of tungsten in solution (Mallory-1000 was analyzed for tungsten, its major constituent). The tungsten specimen lost 3.1 milligrams by the weight change method and 36 milligrams using the colorimetric method. Cadmium gained 3.9 milligrams by the weight change method. Colorimetric analysis of the water gave 8.4 milligrams of cadmium in solution. See table II for comparison of data. The data in table II clearly indicate that the measurement of weight change does not give sufficient information concerning metal ions in solution for nuclear

TABLE II. - COMPARISON OF WEIGHT CHANGE METHOD AND COLORIMETRIC ANALYSES OF IMMERSION WATER FOR DETERMINING CORROSION

Metal ion	Duration of test, days	By weighing specimen before and after	By colorimetric analyses of immersion water
		Weight change, mg	
Copper	34	-0.5	-2.4
Cadmium	9	3.9	-8.4
Tungsten	34	-3.1	-36
Tungsten (from Mallory-1000)	34	-304	-340

application. These data are important when activation of the ions can cause high radiation levels.

A related reactor application problem was experienced at the 60-megawatt Plum Brook Reactor. Tungsten-187 activity levels of 10^6 to 10^7 disintegrations per minute per milliliter were present in the reactor coolant. These tungsten activity levels were intolerable. The chemical concentration of the tungsten in the reactor coolant ranged from 4 to 50 parts per billion (ppb). Tungsten atoms entered the coolant as a result of corrosion of a remote Mallory-1000 gamma shield. The mechanism which produced the high activity level of tungsten-187 was the deposition of circulating tungsten in-pile on the aluminum surfaces of the fuel elements. The tungsten was then activated. The majority of tungsten-187 atoms entered the coolant by recoil. Removal of the shield eliminated the high activity problem.

Titanium, 304 stainless steel, 1100 aluminum, tantalum, silver, and boron steel showed no detectable metal ions in solution after a minimum of 1 week immersion.

SUMMARY AND CONCLUSIONS

The corrosion of 10 metals and alloys in deionized water at 38° C was determined. Titanium, 1100 aluminum, 304 stainless steel, boron steel, silver, and tantalum showed no corrosion in deionized water. Cadmium, Mallory-1000, tungsten, and copper exhibit corrosion at this temperature. In nuclear applications, chemical analyses of the water in which test specimens are immersed provide more useful corrosion information than does physical measurement of weight loss.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, March 10, 1969,
122-29-05-13-22.

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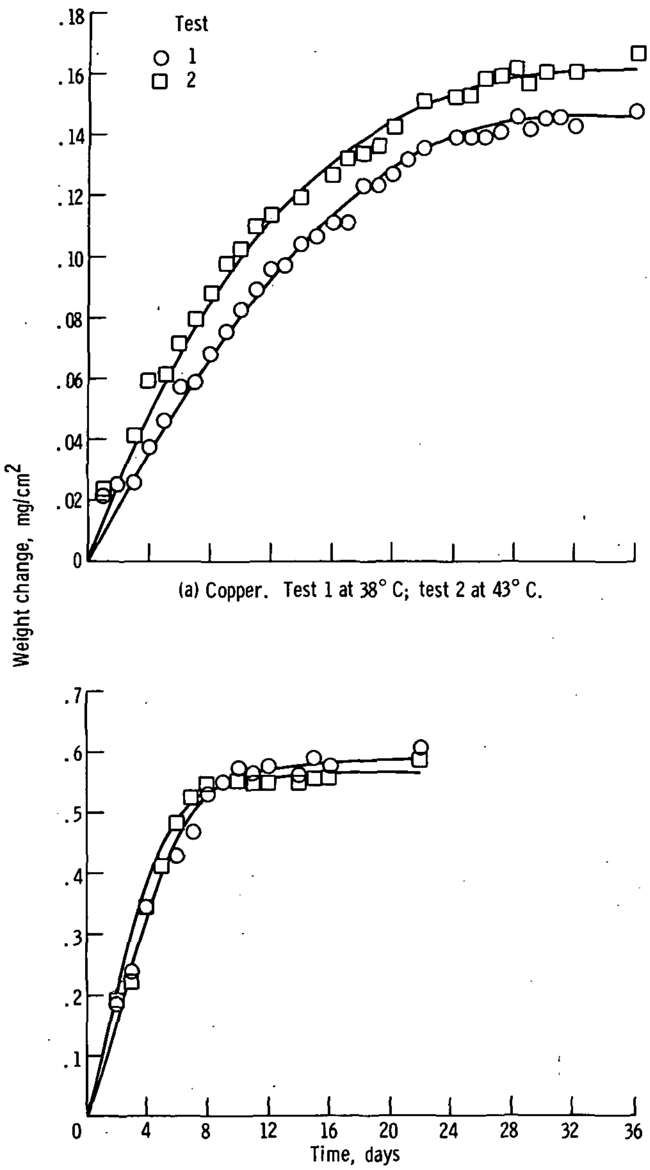
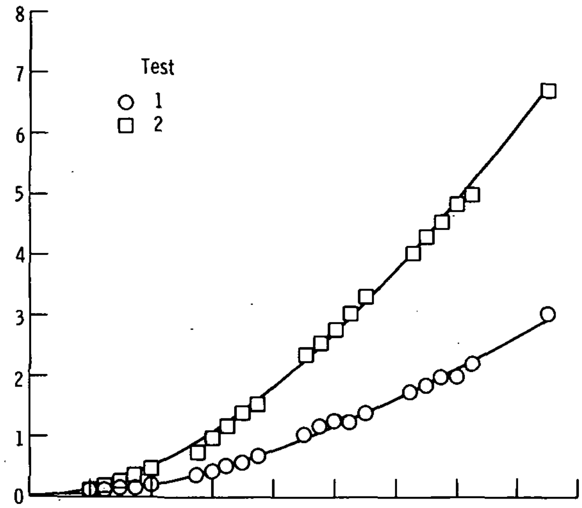


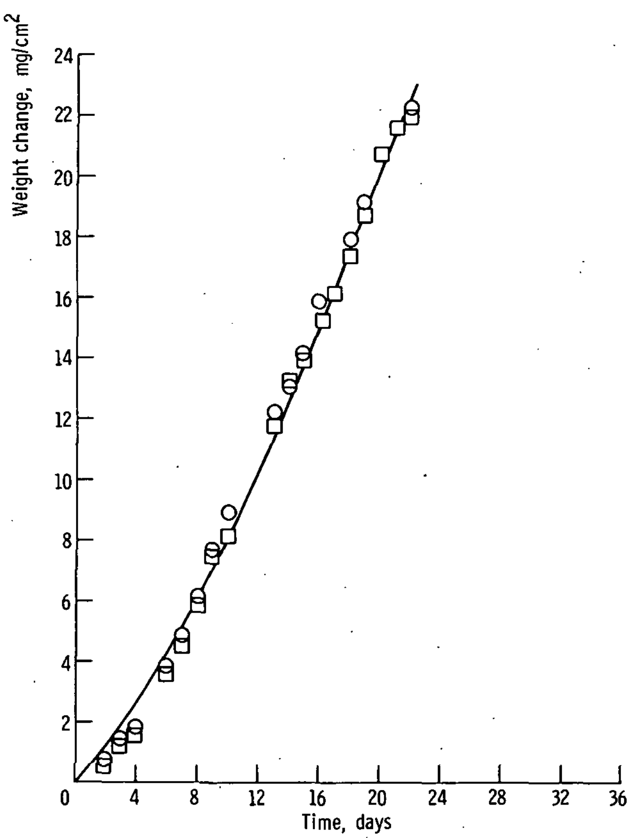
(a) Copper. Test 1 at 38° C; test 2 at 43° C.

(b) Cadmium. Test temperature, 38° C.

Figure 1. - Weight per square centimeter released to deionized water.



(c) Tungsten. Test temperature, 38° C.



(d) Tungsten from Mallory-1000. Test temperature, 38° C.

Figure 1. - Concluded.

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